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(54) Title: POLISHING SLURRIES FOR COPPER AND ASSOCIATED MATERIALS

(57) Abstract: A chemical mechanical polishing slurry and method for using the slurry for polishing copper, barrier material and dielectric material that comprises a first and second slurry. The first slurry has a high removal rate on copper and a low removal rate on barrier material. The second slurry has a high removal rate on barrier material and a low removal rate on copper and dielectric material. The first and second slurries at least comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a cleaning agent.

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**POLISHING SLURRIES FOR COPPER
AND ASSOCIATED MATERIALS**

BACKGROUND OF THE INVENTION

The present invention relates to a chemical mechanical polishing slurry for surfaces of a semiconductor wafer, and more particularly, to a chemical mechanical polishing slurry and a method for using the slurry to remove and polish copper, barrier materials and dielectric materials layered on semiconductor wafer surfaces.

Semiconductor wafers are used to form integrated circuits. The semiconductor wafer typically includes a substrate, such as silicon, upon which dielectric materials, barrier materials, and metal conductors and interconnects are layered. These different materials have insulating, conductive or semi-conductive properties. Integrated circuits are formed by patterning regions into the substrate and depositing thereon multiple layers of dielectric material, barrier material, and metals.

In order to obtain the correct patterning, excess material used to form the layers on the substrate must be removed. Further, to obtain efficient circuits, it is important to have a flat or planar semiconductor wafer surface. Thus, it is necessary to polish certain surfaces of a semiconductor wafer.

Chemical Mechanical Polishing or Planarization ("CMP") is a process in which material is removed from a surface of a semiconductor wafer, and the surface is polished (planarized) by coupling a physical process such as abrasion with a chemical process such as oxidation or chelation. In its most rudimentary form, CMP involves applying slurry, a solution of an abrasive and an active chemistry, to a polishing pad that buffs the surface of a semiconductor wafer to achieve the removal, planarization, and polishing

1 process. It is not desirable for the removal or polishing process to be comprised of purely
2 physical or purely chemical action, but rather the synergistic combination of both in order
3 to achieve fast uniform removal. In the fabrication of integrated circuits, the CMP slurry
4 should also be able to preferentially remove films that comprise complex layers of metals
5 and other materials so that highly planar surfaces can be produced for subsequent
6 photolithography, or patterning, etching and thin-film processing.

7 Recently, copper has been used as the metal interconnect for semiconductor
8 wafers. Typically for copper technology, the layers that are removed and polished
9 consist of a copper layer (about 1-1.5 μm thick) on top of a thin copper seed layer (about
10 0.05-0.15 μm thick). These copper layers are separated from the dielectric material
11 surface by a layer of barrier material (about 50-300 \AA thick). The key to obtaining good
12 uniformity across the wafer surface after polishing is by using a slurry that has the correct
13 removal selectivities for each material. If appropriate material removal selectivity is not
14 maintained, unwanted dishing of copper and/or erosion of the dielectric material may
15 occur.

16 Dishing occurs when too much copper is removed such that the copper surface is
17 recessed relative to the dielectric surface of the semiconductor wafer. Dishing primarily
18 occurs when the copper and barrier material removal rates are disparate. Oxide erosion
19 occurs when too much dielectric material is removed and channels are formed in the
20 dielectric material on the surface of the semiconductor wafer relative to the surrounding
21 regions. Oxide erosion occurs when the dielectric material removal rate is locally much
22 higher than the copper removal rate. Dishing and oxide erosion are area dependent being
23 wafer pattern and pitch dependent as well.

1 Typical commercial CMP slurries used to remove overfill material and polish
2 semiconductor wafer surfaces have a barrier material removal rate below 500 Å/min.
3 Further, these slurries have a copper to barrier material removal rate selectivity of greater
4 than 4:1. This disparity in removal rates during the removal and polishing of the barrier
5 material results in significant dishing of copper on the surface of the semiconductor wafer
6 and/or poor removal of the barrier material.

7 Another problem with conventional CMP slurries is that the removal chemistry of
8 the slurry is compositionally unstable. Further, many of the colloidal abrasives
9 agglomerate after relatively short time frames following addition to the supporting
10 chemistry. Both of these problems lead to significant operational obstacles.

11 A further problem in commercial CMP slurries is that the abrasive materials in the
12 slurries produce defects in the form of micro scratches. These slurries also have poor
13 planarization efficiency, which is the ability of the slurry to polish high points
14 preferentially over low points on the surface of the wafer. Micro scratches and poor
15 planarization efficiency result in integrated circuits with increased defects and a lower
16 yield.

17 Still another problem of commercial CMP slurries is that the chemicals that make
18 up the slurries produce a copper surface that has a high corrosion tendency post polish.

19 An object of this invention, therefore, is a CMP slurry that employs a two-step
20 slurry approach. The slurry used in the first step has a high copper removal rate and a
21 comparatively low barrier material removal rate. The slurry used in the second step has a
22 relatively high barrier material removal rate, comparable removal rate for copper and low
23 removal rate on the dielectric material. By using this two-step slurry approach, the first

1 and second slurries can provide the appropriate selectivity ranges to minimize copper
2 dishing and oxide erosion, thereby providing a viable CMP approach to advanced device
3 manufacturing.

4 Another object of the invention is for the first and second slurries to have stable
5 removal chemistry.

6 Yet another object is to use abrasives in the first slurry that achieve high copper
7 removal rates, but minimal barrier material removal rates, and to use abrasives in the
8 second slurry that provide superior removal rates on barrier material and low removal
9 rates for copper, which also minimize micro scratch defects and provide very good
10 planarization efficiency.

11 It is a further object of this invention to employ active copper cleaning chemistry
12 and corrosion inhibitors in the slurry to minimize copper corrosion post polish, and to
13 eliminate post-polish cleaning steps.

14 These and other objects and advantages of the invention will be apparent to those
15 skilled in the art upon reading the following detailed description and upon reference to
16 the drawings.

17 SUMMARY OF THE INVENTION

18 The present invention is directed to a chemical mechanical polishing slurry
19 comprising a first slurry, which has a high removal rate on copper and a low removal rate
20 on barrier material and a second slurry, which has a high removal rate on barrier material
21 and a low removal rate on copper and the associated dielectric material. The first and
22 second slurries comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a
23 cleaning agent. Also disclosed as the present invention is a method for chemical

1 mechanical polishing copper, barrier material and dielectric material with the polishing
2 slurry of the present invention. As will become apparent from the discussion that
3 follows, the stable slurry and method of using the slurry provide for removal of material
4 and polishing of semiconductor wafer surfaces with significantly no dishing or oxide
5 erosion, with significantly no surface defects and good planarization efficiency, and
6 produce a copper surface with minimal corrosion tendency post-polish.

7 BRIEF DESCRIPTION OF THE DRAWINGS

8 FIG. 1 is a cross-sectional view of a semiconductor wafer prior to chemical
9 mechanical polishing.

10 FIG. 2 is a cross sectional view of the semiconductor wafer of FIG. 1 following
11 chemical mechanical polishing with the first slurry, according to the present invention.

12 FIG. 3 is a cross sectional view of the semiconductor wafer of FIG. 2 following
13 chemical mechanical polishing with the second slurry, according to the present invention.

14 FIG. 4 is a cross sectional view of a semiconductor wafer illustrating copper
15 dishing.

16 FIG. 5 is a cross sectional view of a semiconductor wafer illustrating oxide
17 erosion.

18 FIG. 6 is a transmission electron micrograph (TEM) showing 13 nm silica
19 particles of the present invention.

20 FIG. 7 is the size distribution of 13nm silica particles of the present invention
21 determined with Coulter N4 Plus particle analyzer.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 illustrates a semiconductor wafer **10** prior to CMP. As shown, substrate **11** may be made of any conventional semiconductor materials, including silicon or germanium or silicon-germanium. Layered on top of the substrate **11** is dielectric material **12**, which is preferentially silicon oxide, low k dielectrics comprised substantially of silicon oxide or a carbon containing silicon oxide. The instant invention is not limited to such dielectric materials and is also useful for removal of dielectrics such as fluoride doped silicon glass (FSG). Layered on the dielectric material **12**, is barrier material **13**. The barrier material layer **13** is typically about 50 to 300 Å thick. The barrier material **13** may be any material conventionally used, but is typically chosen from the group of tungsten nitride, tantalum, tantalum nitride, titanium nitride, silicon doped tantalum nitride or silicon doped titanium nitride. Finally, a layer of copper **14** covers the barrier material layer **13**, and extends into trenches **14a**, **14b**, and **14c**. The copper layer **14** is usually about 0.1-0.15 µm thick and the copper layer **14** in **FIG. 1** includes a thin copper seed layer, which is usually about 0.05-0.15 µm thick.

The invention is a CMP slurry designed to polish copper **14** and associated barrier materials **13** such as tungsten nitride, tantalum, tantalum nitride, silicon doped tantalum nitride, titanium nitride and silicon doped titanium nitride. The chemical mechanical polishing slurry of the present invention is comprised of two parts. The first slurry is a copper selective slurry used to remove the bulk copper down to the barrier layer (**FIG. 2**). The first slurry has a high removal rate of copper and a low removal rate of barrier material. The second slurry is selective to the barrier layer and removes the barrier material down to the dielectric material. The barrier and copper rate are comparable for

this step (FIG. 3). The various removal rates of the first and second slurries on various materials are shown in Table 1. In this way, two slurries together comprise a combined package to polish copper metallization schemes for integrated circuit manufacturing.

Table 1. Removal Rates of the First and Second Slurries on Different Materials*

LAYER	First Slurry Removal Rates (Å/min)	Second Slurry Removal Rates (Å/min)	Selectivity Material:Cu	
			First Slurry	Second Slurry
Copper	>5000	<1000		
Tantalum	< 500	> 1000	1:10	1:1
Tantalum Nitride	< 500	> 1000	1:10	1:1
Thermal Oxide	< 150	< 150	1:50	1:6

*(Down Force = 5 psi, Flow Rate = 200 mL/min, Table Speed = 90 rpm, Quill Speed = 50 rpm, Pad Type = IC 1000)

Referring to FIG. 1, the present invention includes a method for chemical mechanical polishing copper 14, barrier material 13 and dielectric material 12, comprises the following steps: (1) providing a first chemical mechanical polishing slurry that has a high removal rate on copper 14 and a low removal rate on barrier material 13; (2) chemical mechanical polishing a semiconductor wafer surface 10 with the first slurry; (3) providing a second chemical mechanical polishing slurry that has a high removal rate on barrier material 13 a comparable removal rate on copper 14 and a low removal rate on the dielectric material 12; and (4) chemical mechanical polishing the semiconductor wafer surface 10 with the second slurry.

Generally, the slurry is applied to a pad contained on a polishing instrument. Polishing instrument parameters such as down force (DF), flow rate (FR), table speed

1 (TS), quill speed (QS), and pad type can be adjusted to effect the results of the CMP
2 slurry. These parameters are important in obtaining efficient planarization results and
3 limiting dishing and erosion. Although these parameters may be altered, when used with
4 the CMP slurry of the present invention, the standard conditions used are DF of 5psi, FR
5 of 200 mL/min, TS of 90 rpm, QS of 50 rpm, and the IC 1000 pad type.

6 **FIG. 2** illustrates the semiconductor wafer **10** of **FIG. 1**, after steps (1) and (2) of
7 the present method for CMP have been carried out, and the semiconductor wafer surface
8 has been polished with the first slurry. When **FIG. 2** is compared to **FIG. 1**, the top
9 copper layer **14** in **FIG. 1** has been preferentially removed, and only the copper in the
10 trenches (**FIG. 2**) **18a**, **18b**, and **18c** is left. As shown in **FIG. 2** the barrier material layer
11 **17** is substantially in tact, and the dielectric material **16** based on substrate **15** is still
12 unexposed.

13 Similarly, **FIG. 3** illustrates the semiconductor wafer **10** of **FIGS. 1** and **2**, after
14 steps (3) and (4) of the present method for CMP have been carried out, and the
15 semiconductor wafer surface has been polished with the second slurry. As shown in
16 **FIG. 3**, the barrier material layer **21** has been removed down to the dielectric material **20**.
17 The second slurry also removed just enough of the copper in trenches **22a**, **22b**, and **22c**
18 so that the surface of the semiconductor wafer **10** is flat and planar. The second slurry
19 also serves to polish the newly exposed surface, including the dielectric material **20**, the
20 barrier material **21a**, **21b**, **21c**, and the copper **22a**, **22b**, **22c**. All of these materials are
21 based on substrate **19**.

22 By using the first and second slurries of the claimed invention, with the
23 selectivities described in Table 1, and following the described method, copper dishing

(FIG. 4) and oxide erosion (FIG. 5) can be minimized. FIG. 4 shows a semiconductor wafer to which a CMP slurry has been applied, which had a higher selectivity for copper 26a, 26b, 26c than for the barrier material 25a, 25b, 25c or dielectric material 24. As a result, disparate amounts of copper are removed from the surface of the semiconductor wafer. This is known as copper dishing and is shown by the dish-like troughs 27a, 27b, and 27c in the trenches of copper 26a, 26b, 26c. The CMP slurry of the present invention and method of using this slurry greatly reduces copper dishing.

Similarly, FIG. 5 shows a semiconductor wafer to which a CMP slurry has been applied, which has a higher selectivity for the dielectric material 29 than for the barrier material 30a, 30b, 30c, or copper 31a, 31b, 31c. As a result, disparate amounts of dielectric material are removed from the surface of the semiconductor wafer. This is known as oxide erosion and is shown by the indentions and/or reduction of the dielectric material 29a, 29b. The CMP slurry of the present invention and method of using this slurry greatly reduces oxide erosion.

Turning now to the composition of the CMP slurry, generally the first and second slurries comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a cleaning agent. The chemistry of the first and second slurries should be stable and have a pH in the range of about 2 to 5. The first and second slurries may contain potassium or ammonium hydroxide in such amounts to adjust the pH to a range of about 2 to 5

The preferred oxidizing agent for the first and second slurries is potassium iodate formed by reaction of HIO_3 with KOH. The corrosion inhibitor and cleaning agent for the first and second slurries should be a carboxylic acid. More specifically, the carboxylic acid may be chosen from the group of glycine, oxalic acid, malonic acid,

1 succinic acid and nitrilotriacetic acid. Alternatively, the carboxylic acid may be a
2 dicarboxylic acid that preferentially has a nitrogen containing functional group. In the
3 most preferred form, the corrosion inhibitor and cleaning agent for the first and second
4 slurries is iminodiacetic acid. Inorganic acids such as phosphoric, nitric and hydrochloric
5 were added to adjust pH and accelerate copper removal rates.

6 The use of potassium iodate as the oxidizing agent and carboxylic acids as the
7 corrosion inhibitors and cleaning agents and inorganic acids as accelerating agents
8 creates a stable removal chemistry in the pH region of about 2 to 5, for the first and
9 second slurries. Further, the use of copper corrosion inhibitors and cleaning agents
10 minimizes copper corrosion, as indicated by low static etch rates of roughly less than 50
11 Å/min on copper.

12 The silica particles of the first and second slurries can be precipitated. The
13 precipitated particles usually range from about 3 to 100 nm in size and can be spherical.
14 An alternative to precipitated silica particles in the first slurry is fumed silica. Generally,
15 the fumed silica has a mean particle size of less than 700 nm.

16 Alternatively, and more preferred is to use colloidal silica particles of the type
17 described. The colloidal silica particles can range from about 3 to 100 nm in size, and
18 can be spherical. Preferentially, when the first and second slurries employ spherical
19 colloidal particles, the particles should have a narrow size distribution. More
20 specifically, about 99.9% of the spherical colloidal particles should be within about 3
21 sigma of a mean particle size with negligible particles larger than about 500 nm.

22 The first slurry, thus, can employ either precipitated spherical silica particles in
23 the size range of 3 to 100 nm, or fumed silica with mean particle size less than about 700

1 nm. These particles coupled with the iodate chemistry allows the first slurry to achieve
2 high copper removal rate but minimal barrier material removal rate. Colloidal silica, with
3 a narrow size distribution, minimizes micro scratch defects and provides superior
4 removal rates on barrier materials, greater than about 1000 Å/min, and low removal rates
5 for copper for the second slurry. Further, spherical silica abrasives with a mean size of
6 less than about 100 nm provide very good planarization efficiency.

7 The pH, oxidizing agents, modifying agents, abrasive particle composition and
8 size distribution, and weight percent were evaluated to establish a baseline for removal
9 rates and selectivity.

10 EXAMPLE I

11 Precipitated silica mean particle sizes of 8 nm, 20 nm, and 70 nm were tested.
12 The fumed silica particle size tested was less than 700 nm. The optimum CMP slurry,
13 including the first and second slurry, had a precipitated silica mean size of less than about
14 100 nm. The optimum fumed silica abrasive mean size for the first slurry is less than
15 about 700 nm. The optimum CMP slurry formulations contain 1-10% precipitated silica,
16 or fumed silica for the first slurry.

17 Further, different types of abrasive particles were studied to maximize the
18 removal and selectivity characteristic of the slurry. Precipitated silica abrasives, with
19 mean size distributions of 4 nm, 8 nm, 13 nm, 20 nm and 70 nm were tested. FIG. 6
20 shows a TEM picture of 13 nm slurry. The size distribution of these particles is
21 presented in FIG. 7. Fumed silica, with a mean particle size of less than about 700 nm,
22 was also evaluated. All of these mean size distributions can be used to achieve effective
23 polishing rates and selectivities for the first and second slurries.

EXAMPLE 2

Different pH ranges were tested for the first and second slurries (See Table 2 and 3). The precipitated silica abrasives had a starting pH range of 9-11 and the fumed silica had a starting pH range of 2-7. The optimum CMP slurry was found to be acidic. Thus, the pH ranges were altered to the 2 to 5 range by adding potassium, sodium or ammonium hydroxide in appropriate amounts to solutions of iodic acid, cleaning agent and corrosion inhibitor.

EXAMPLE 3

Several formulations of the first slurries were prepared. The characteristics of these formulations are described in Table 2. The first slurry is optimally comprised of formula 5, for colloidal silica particles, and formula 19 for fumed silica particles. Thus, the first slurry is preferentially comprised of 1-10% colloidal silica with particle size 3 to 100 nm, or 1-5% fumed silica with mean particle size of less than about 700 nm. Further, the active chemistry for the optimum first slurry is about 1-12% potassium iodate (KIO_3 , formed by reaction of HIO_3 with KOH), which is used as the oxidizing agent for the copper, about 0-5% concentrated inorganic acid as a copper activating agent, and 0-2% iminodiacetic acid (IDA) as the copper corrosion inhibitor and cleaning agent.

Table 2. Formulations for the First Slurry

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
1	HIO_3 , 8.22	IDA, 1.5	H_3PO_4 , 1.764	KOH 4.523; NH_4OH , 3.7768	Colloidal (13 nm), 1	2.4	-	3176	-	-
2	HIO_3 , 12.33	IDA, 1.5	H_3PO_4 , 0.5	KOH, 5.022	Colloidal (13 nm)k 1	2.7	113	4713	-	-
3	HIO_3 , 10	IDA, 1.5	-	NH_4OH , 2.685	Colloidal (13 nm), 1	3.0	126	4800	-	-
4	HIO_3 , 10	IDA, 1.5	-	KOH, 4.084	Colloidal (13 nm), 1	2.8	126	5165	-	-

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
5!	HIO ₃ , 10	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 4.523	Colloidal (13 nm), 1	2.9	151	6530	453	590
6	HIO ₃ , 12.33	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 5.486	Colloidal (13 nm), 1	3.1	115	6877	422	528
7	HIO ₃ , 12.33	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 5.486	Colloidal (13 nm), 1	3.1	115	6877	422	528
8	HIO ₃ , 8.22	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 3.978	Colloidal (13 nm), 1	3.1	112	4797	494	730
9	HIO ₃ , 8.22	-	HCl, 0.15g	KOH, 4.284	Colloidal (13 nm), 1	6.0	117	423	878	1031
10	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 2.92	Colloidal (13 nm), 1	3.4	134	2138	550	618
11	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 2.92	Colloidal (13 nm), 1	3.6	105	2134	512	882
12	HIO ₃ , 6.17	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 4.087	Colloidal (13 nm), 1	6.0	106	1448	890	1047
13	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 2.918	Colloidal (13 nm), 1	3.5	140	3900	720	1066
14	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 3.012	Colloidal (8 nm), 1	3.6	45	4157	527	623
15	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 3.067	Colloidal (20 nm), 1	3.7	172	6852	649	842
16	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 3.13	Colloidal (70 nm), 1	3.6	171	2720	451	625
17	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 2.918	Colloidal (13 nm), 1	3.6	118	3973	832	1028
18	HIO ₃ , 4.11	IDA, 1.5	-	KOH, 2.474	Colloidal (13 nm), 1	3.5	167	5630	728	946
19!	HIO ₃ , 4.11	IDA, 1.5	H ₃ PO ₄ , 0.5	KOH, 2.918	fumed, 1	3.6	15	4823	2.4	-10

* "RR" means removal rates in Å/min.

Stock Solutions: HIO₃ (50% by weight); H₃PO₄ (85.87% by weight); KOH (45-46% by weight);
NH₄OH (28-30% by weight); HNO₃ (68-70% by weight); HCl (36-38% by weight)

As can be seen from Table 2, all of the first slurry formulations of the present invention were effective in achieving acceptable copper removal rates, and semiconductor wafer surfaces of high quality. Thus, the first slurry is preferentially comprised of 1-10% colloidal silica with particle size of less than about 100 nm.

EXAMPLE 4

Several formulations of the second slurry were prepared. The characteristics of these formulations are described in Table 3. The second step slurry is dependent on the copper removal rate requirement and therefore is optimally comprised of either formula 6 or 9. The active chemistry for the optimum second slurry is 0.1-1% potassium iodate (KIO_3 , formed by reaction of HIO_3 with KOH) as the oxidizing agent for the copper, 0-5 % concentrated inorganic acid and 0-2% iminodiacetic acid as the copper corrosion inhibitor and cleaning agent. Table 3. Formulations for the Second Slurry

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
1	HIO_3 , 0.1	IDA, 1.5	-	KOH 1.005	Colloidal (13 nm), 1	3.4	101	430	462	2128
2	HIO_3 , 0.1	IDA, 1.5	HNO_3 , 10	KOH 13.66	Colloidal (13 nm), 1	3.0	100	572	146	1749
3	HIO_3 , 0.1	IDA, 0.1	HNO_3 , 5; HCl , 5	KOH 13.14	Colloidal (13 nm), 1	3.0	53	358	50.21	751
4	HIO_3 , 0.1	IDA, 1.5	H_3PO_4 , 1.5	KOH 2.079	Colloidal (13 nm), 1	2.7	116	574	772	1471
5	HIO_3 , 0.1	IDA, 1.5	HNO_3 , 2	KOH 3.674	Colloidal (13 nm), 1	3.1	149	511	670	2087
6	HIO_3 , 0.1	IDA, 1.5	HNO_3 , 2.31	NH_4OH , 2.507	Colloidal (13 nm), 1	3.1	130	239	623	2146
7	HIO_3 , 0.1	IDA, 1.5	-	KOH , 1.312	Colloidal (13 nm), 1	3.4	126	1053	657	1200
8	HIO_3 , 0	IDA, 2	-	KOH , 1.305	Colloidal (13 nm), 1	3.5	200	0	> 3000	217
9	HIO_3 , 0.5	IDA, 1.5	-	KOH , 1.086	Colloidal (13 nm), 1	3.5	120	1120	731	907
10	HIO_3 , 1.5	IDA, 1.5	-	KOH , 1.443	Colloidal (13 nm), 1	3.5	131	1208	901	856

* "RR" means removal rates in Å/min.

Stock Solutions: HIO_3 (50% by weight); H_3PO_4 (85.87% by weight); KOH (45-46% by weight); NH_4OH (28-30% by weight); HNO_3 (68-70% by weight); HCl (36-38% by weight).

As can be seen from Table 3, all of the second slurry formulations of the present invention were effective in achieving acceptable barrier dielectric and copper removal rates, and semiconductor wafer surfaces of high quality.

1 The first and second slurries described herein, may also be used in a method of
2 chemical mechanical polishing as described above. Also, while this invention has been
3 disclosed and discussed primarily in terms of specific embodiments thereof, it is not
4 intended to be limited thereto. Other modifications and embodiments will be apparent to
5 the worker in the art.

1 **WHAT IS CLAIMED IS:**

2 1. A method for chemical mechanical polishing copper, barrier material and
3 dielectric material, the method which comprises the steps of:

4 a) providing a first chemical mechanical polishing slurry wherein said first
5 slurry has a high removal rate on copper and a low removal rate on said barrier material;

6 b) chemical mechanical polishing a semiconductor wafer surface with said
7 first slurry;

8 c) providing a second chemical mechanical polishing slurry wherein said
9 second slurry has a high removal rate on said barrier material, comparable removal rate
10 on copper and low removal rate on said dielectric material; and

11 d) chemical mechanical polishing said semiconductor wafer surface with said
12 second slurry.

13 2. The method of claim 1 wherein said first slurry has a copper removal rate of
14 greater than about 5000 Å/min and a barrier material removal rate of less than about 500
15 Å/min.

16 3. The method of claim 1 wherein said first slurry comprises about 1-10% colloidal
17 silica, about 1-12% potassium iodate, about 0-5% concentrated inorganic acid, and about
18 0-2% iminodiacetic acid.

19 4. The method of claim 1 wherein said first slurry comprises about 1-5% fumed
20 silica, about 1-12% potassium iodate, about 0-5% concentrated inorganic acid, and about
21 0-2% iminodiacetic acid.

22 5. The method of claim 3 wherein said colloidal silica has a particle size of about 3
23 to 100 nm.

- 1 6. The method of claim 4 wherein said fumed silica has a mean particle size of less
2 than about 700 nm.
- 3 7. The method of claim 3 wherein said first slurry further comprises potassium,
4 sodium or ammonium hydroxide in such amounts to modify the pH to a region of about 2
5 to 4.
- 6 8. The method of claim 4 wherein said first slurry further comprises potassium,
7 sodium or ammonium hydroxide in such amounts to modify the pH to a region of about 2
8 to 4.
- 9 9. The method of claim 1 wherein said second slurry has a barrier material removal
10 rate of greater than about 1000 Å/min and a copper removal rate of less than about 1000
11 Å/min and dielectric material removal rate of < 500 Å/min.
- 12 10. The method of claim 1 wherein said second slurry comprises about 1-10%
13 colloidal silica, about 0.1-1% potassium iodate, 0-5 % concentrated inorganic acid and
14 about 0-2% iminodiacetic acid.
- 15 11. The method of claim 10 wherein said colloidal silica has a particle size of less
16 than about 100 nm.
- 17 12. The method of claim 10 wherein said second slurry further comprises potassium,
18 sodium or ammonium hydroxide in such amounts to modify the pH to a region of about 2
19 to 5.
- 20 13. The method of claim 1 wherein said dielectric material is silicon oxide.
- 21 14. The method of claim 1 wherein said barrier material is selected from the group
22 consisting of: tungsten nitride, tantalum, tantalum nitride, silicon doped tantalum nitride,
23 titanium nitride and silicon doped titanium nitride.

- 1 15. The method of claim 1 wherein said first and second slurries are stable and have a
2 pH in the range of from about 2 to 5.
- 3 16. The method of claim 1 wherein said barrier material is tantalum.
- 4 17. The method of claim 1 wherein said barrier material is tantalum nitride or silicon
5 doped tantalum nitride.
- 6 18. The method of claim 16 wherein said first slurry has a copper removal rate of
7 greater than about 5000 Å/min and a tantalum removal rate of less than about 500 Å/min
8 and said second slurry has a tantalum removal rate of greater than about 1000 Å/min and
9 a copper removal rate of less than about 1000 Å/min and a dielectric material removal
10 rate of < 500 Å/min.
- 11 19. The method of claim 17 wherein said first slurry has a copper removal rate of
12 greater than about 5000 Å/min and a tantalum nitride removal rate of less than about 500
13 Å/min and said second slurry has a tantalum nitride removal rate of greater than about
14 1000 Å/min and a copper removal rate of less than about 1000 Å/min and a dielectric
15 material removal rate of < 500 Å/min.
- 16 20. The method of claim 1 wherein said first and second slurries comprise an
17 oxidizing agent.
- 18 21. The method of claim 20 wherein said oxidizing agent is an iodate salt.
- 19 22. The method of claim 1 wherein said first and second slurries comprise a corrosion
20 inhibitor.
- 21 23. The method of claim 1 wherein said first and second slurries comprise a cleaning
22 agent.
- 23 24. The method of claim 22 wherein said corrosion inhibitor is a carboxylic acid.

1 25. The method of claim 24 wherein said carboxylic acid is chosen from the group
2 consisting of: glycine, oxalic acid, malonic acid, succinic acid and nitrilotriacetic acid.

3 26. The method of claim 22 wherein said corrosion inhibitor is a dicarboxylic acid.

4 27. The method of claim 26 wherein said dicarboxylic acid has a nitrogen containing
5 functional group.

6 28. The method of claim 27 wherein said dicarboxylic acid is iminodiacetic acid.

7 29. The method of claim 23 wherein said cleaning agent is a carboxylic acid.

8 30. The method of claim 29 wherein said carboxylic acid is chosen from the group
9 consisting of: glycine, oxalic acid, malonic acid, succinic acid and nitrilotriacetic acid.

10 31. The method of claim 23 wherein said cleaning agent is a dicarboxylic acid.

11 32. The method of claim 31 wherein said dicarboxylic acid has a nitrogen containing
12 functional group.

13 33. The method of claim 32 wherein said dicarboxylic acid is iminodiacetic acid.

14 34. The method of claim 1 wherein said first slurry comprises colloidal silica
15 particles.

16 35. The method of claim 34 wherein said colloidal silica particles are about 3 to 100
17 nm in size.

18 36. The method of claim 34 wherein said colloidal silica particles are spherical.

19 37. The method of claim 35 wherein said colloidal silica particles are spherical

20 38. The method of claim 1 wherein said first slurry comprises fumed silica.

21 39. The method of claim 38 wherein said fumed silica has a mean particle size of less
22 than about 700 nm.

- 1 40. The method of claim 1 wherein said first slurry comprises colloidal silica
2 particles.
- 3 41. The method of claim 40 wherein said colloidal silica particles are about 3 to 100
4 nm in size.
- 5 42. The method of claim 40 wherein said colloidal silica particles are spherical.
- 6 43. The method of claim 41 wherein said colloidal silica particles are spherical.44.
- 7 44. The method of claim 42 wherein said particles have a narrow size distribution.
- 8 45. The method of claim 42 wherein about 99.9% of said particles are within about 3
9 sigma of a mean particle size with negligible particles larger than about 500 nm.
- 10 46. The method of claim 1 wherein said second slurry comprises colloidal silica
11 particles.
- 12 47. The method of claim 46 wherein said colloidal silica particles are about 3 to 100
13 nm in size.
- 14 48. The method of claim 46 wherein said colloidal silica particles are spherical.
- 15 49. The method of claim 47 wherein said colloidal silica particles are spherical.
- 16 50. The method of claim 1 wherein said second slurry comprises colloidal silica
17 particles.
- 18 51. The method of claim 50 wherein said colloidal silica particles are about 3 to 100
19 nm in size.
- 20 52. The method of claim 50 wherein said colloidal silica particles are spherical.
- 21 53. The method of claim 51 wherein said colloidal silica particles are spherical.
- 22 54. The method of claim 52 wherein said particles have a narrow size distribution.

1 55. The method of claim 52 wherein about 99.9% of said particles are within about 3
2 sigma of a mean particle size with negligible particles larger than about 500 nm.

3 56. The method of claim 1 wherein said first and second slurries comprise silica
4 particles, an oxidizing agent, a cleaning agent and a corrosion inhibitor.

5 57. A chemical mechanical polishing slurry comprising:

6 a first slurry, wherein said first slurry has a high removal rate on copper and a
7 low removal rate on barrier material; and

8 a second slurry, wherein said second slurry has a high removal rate on said
9 barrier material and a low removal rate on copper and dielectric material.

10 58. The chemical mechanical polishing slurry of claim 57, wherein said first and
11 second slurries comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a
12 cleaning agent.

13 59. The chemical mechanical polishing slurry of claim 57, wherein said first slurry
14 has a copper removal rate of greater than about 5000 Å/min and a barrier material
15 removal rate of less than about 500 Å/min.

16 60. The chemical mechanical polishing slurry of claim 57, wherein said second slurry
17 has a barrier material removal rate of greater than about 1000 Å/min and a removal rate
18 of less than about 1000 Å/min and dielectric material removal rate < 500 Å/min.

19 61. The chemical mechanical polishing slurry of claim 57, wherein said dielectric
20 material is silicon oxide.

21 62. The chemical mechanical polishing slurry of claim 57, wherein said barrier
22 material is selected from the group consisting of: tungsten nitride, tantalum, tantalum
23 nitride, silicon doped tantalum nitride, titanium nitride and silicon doped titanium nitride.

1 63. The chemical mechanical polishing slurry of claim 57, wherein said barrier
2 material is tantalum.

3 64. The chemical mechanical polishing slurry of claim 57, wherein said barrier
4 material is tantalum nitride or silicon doped tantalum nitride.

5 65. The chemical mechanical polishing slurry of claim 63, wherein said first slurry
6 has a copper removal rate of greater than about 5000 Å/min and a tantalum removal rate
7 of less than about 500 Å/min, and said second slurry has a tantalum removal rate of
8 greater than about 1000 Å/min and a copper removal rate of less than about 1000 Å/min
9 and a dielectric material removal rate < 500 Å/min.

10 66. The chemical mechanical polishing slurry of claim 64, wherein said first slurry
11 has a copper removal rate of greater than about 5000 Å/min and a tantalum nitride
12 removal rate of less than about 500 Å/min, and said second slurry has a tantalum nitride
13 removal rate of greater than about 1000 Å/min and a copper removal rate of less than
14 about 1000 Å/min and a dielectric material removal rate of < 500 Å/min.

15 67. The chemical mechanical polishing slurry of claim 58, wherein said first and
16 second slurries are stable and have a pH region of about 2 to 5.

17 68. The chemical mechanical polishing slurry of claim 58, wherein said oxidizing
18 agent is an iodate.

19 69. The chemical mechanical polishing slurry of claim 58, wherein said corrosion
20 inhibitor is a carboxylic acid.

21 70. The chemical mechanical polishing slurry of claim 69, wherein said carboxylic
22 acid is chosen from the group consisting of: glycine, oxalic acid, malonic acid, succinic
23 acid and nitrilotriacetic acid.

1 71. The chemical mechanical polishing slurry of claim 58, wherein said corrosion
2 inhibitor is a dicarboxylic acid.

3 72. The chemical mechanical polishing slurry of claim 71, wherein said dicarboxylic
4 acid has a nitrogen containing functional group.

5 73. The chemical mechanical polishing slurry of claim 71 wherein said dicarboxylic
6 acid is iminodiacetic acid.

7 74. The chemical mechanical polishing slurry of claim 58, wherein said cleaning
8 agent is a carboxylic acid.

9 75. The chemical mechanical polishing slurry of claim 74 wherein said carboxylic
10 acid is chosen from the group consisting of: glycine, oxalic acid, malonic acid, succinic
11 acid or nitrilotriacetic acid.

12 76. The chemical mechanical polishing slurry of claim 58 wherein said cleaning agent
13 is a dicarboxylic acid.

14 77. The chemical mechanical polishing slurry of claim 76 wherein said dicarboxylic
15 acid has a nitrogen containing functional group.

16 78. The chemical mechanical polishing slurry of claim 76 wherein said dicarboxylic
17 acid is iminodiacetic acid.

18 79. The chemical mechanical polishing slurry of claim 58, wherein said silica
19 particles are precipitated.

20 80. The chemical mechanical polishing slurry of claim 79, wherein said precipitated
21 silica particles are about 3 to 100 nm in size.

22 81. The chemical mechanical polishing slurry of claim 79 wherein said precipitated
23 silica particles are spherical.

- 1 82. The chemical mechanical polishing slurry of claim 80 wherein said precipitated
2 silica particles are spherical.
- 3 83. The chemical mechanical polishing slurry of claim 58 wherein said silica particles
4 for said first slurry are fumed silica.
- 5 84. The chemical mechanical polishing slurry of claim 82 wherein said fumed silica
6 particles have a mean particle size of less than about 700 nm.
- 7 85. The chemical mechanical polishing slurry of claim 58 wherein said silica particles
8 are colloidal silica particles.
- 9 86. The chemical mechanical polishing slurry of claim 85 wherein said colloidal
10 silica particles are about 3 to 100 nm in size.
- 11 87. The chemical mechanical polishing slurry of claim 85 wherein said colloidal
12 silica particles are spherical.
- 13 88. The chemical mechanical polishing slurry of claim 86 wherein said colloidal
14 silica particles are spherical.
- 15 89. The chemical mechanical polishing slurry of claim 87 wherein said particles have
16 a narrow size distribution.
- 17 90. The chemical mechanical polishing slurry of claim 87 wherein about 99.9% of
18 said particles are within about 3 sigma of a mean particle size with negligible particles
19 larger than about 500 nm.
- 20 91. The chemical mechanical polishing slurry of claim 57 wherein said first slurry
21 comprises about 1-10% colloidal silica, about 1-12% potassium iodate, about 0-5%
22 concentrated inorganic acid, and about 0-2% iminodiacetic acid.

1 92. The chemical mechanical polishing slurry of claim 57 wherein said first slurry
2 comprises about 1-5% fumed silica, about 1-12% potassium iodate, about 0-5%
3 concentrated inorganic acid, and about 0-2% iminodiacetic acid.

4 93. The chemical mechanical polishing slurry of claim 91 wherein said colloidal
5 silica has a particle size of about 3 to 100 nm.

6 94. The chemical mechanical polishing slurry of claim 92 wherein said fumed silica
7 has a mean particle size of less than about 700 nm.

8 95. The chemical mechanical polishing slurry of claim 91 wherein said first slurry
9 further comprises potassium or ammonium hydroxide in such amounts to modify the pH
10 to a region of about 2 to 5.

11 96. The chemical mechanical polishing slurry of claim 92 wherein said first slurry
12 further comprises potassium or ammonium hydroxide in such amounts to modify the pH
13 to a region of about 2 to 5.

14 97. The chemical mechanical polishing slurry of claim 57 wherein said second slurry
15 comprises about 1-10% colloidal silica, about 0.1-1% potassium iodate, and about 0-2%
16 iminodiacetic acid and 0-5 % concentrated inorganic acid.

17 98. The chemical mechanical polishing slurry of claim 97 wherein said colloidal
18 silica has a particle size of less than about 100 nm.

19 99. The chemical mechanical polishing slurry of claim 97 wherein said second slurry
20 further comprises potassium or ammonium hydroxide in such amounts to modify the pH
21 to a region of about 2 to 5.

1 100. The chemical mechanical polishing slurry of claim 91 wherein said second slurry
2 comprises about 1-10% colloidal silica, about 0.1-1% potassium iodate, and about 0-2%
3 iminodiacetic acid and 0-5 % concentrated inorganic acid.

4 101. The chemical mechanical polishing slurry of claim 92 wherein said second slurry
5 comprises about 1-10% colloidal silica, about 0.1-1% potassium iodate, and about 0-2%
6 iminodiacetic acid and 0-5 % concentrated inorganic acid.

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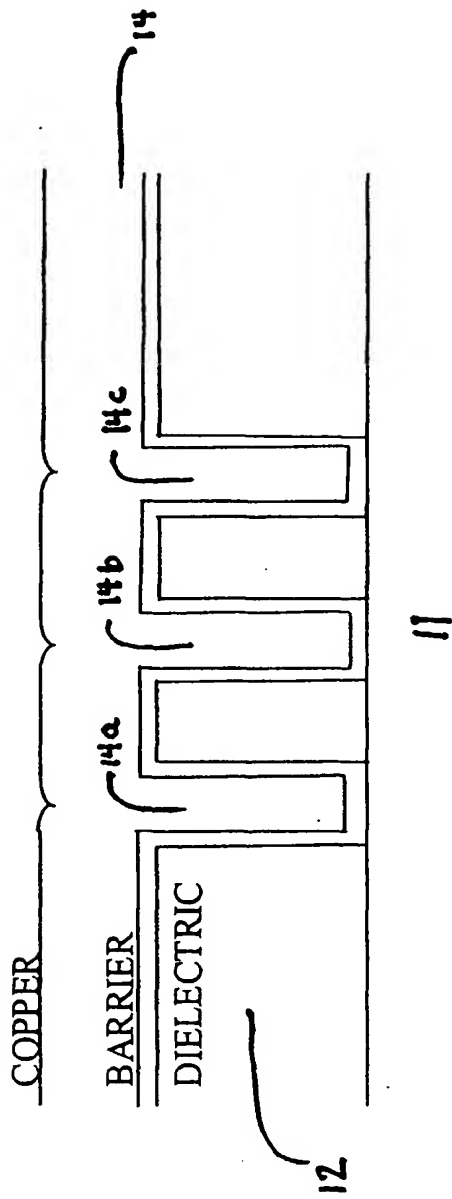


FIG. 1

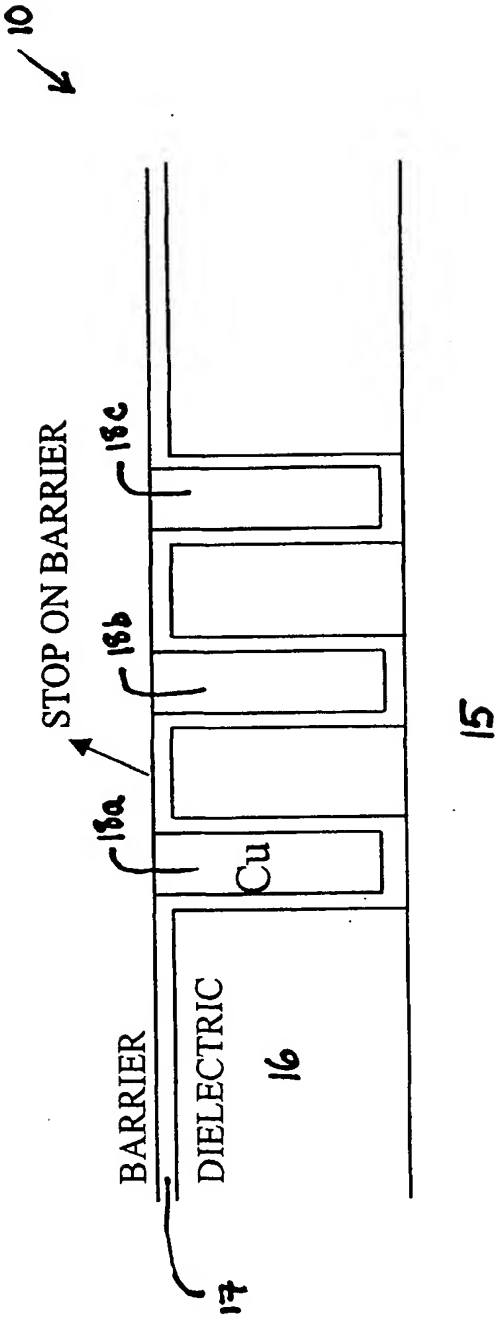


FIG. 2

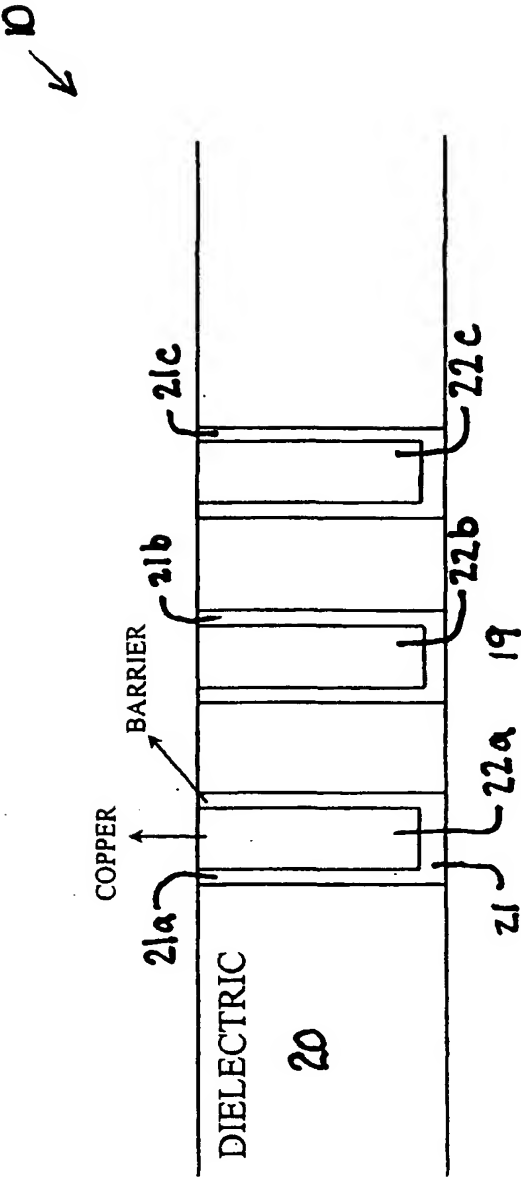


FIG. 3

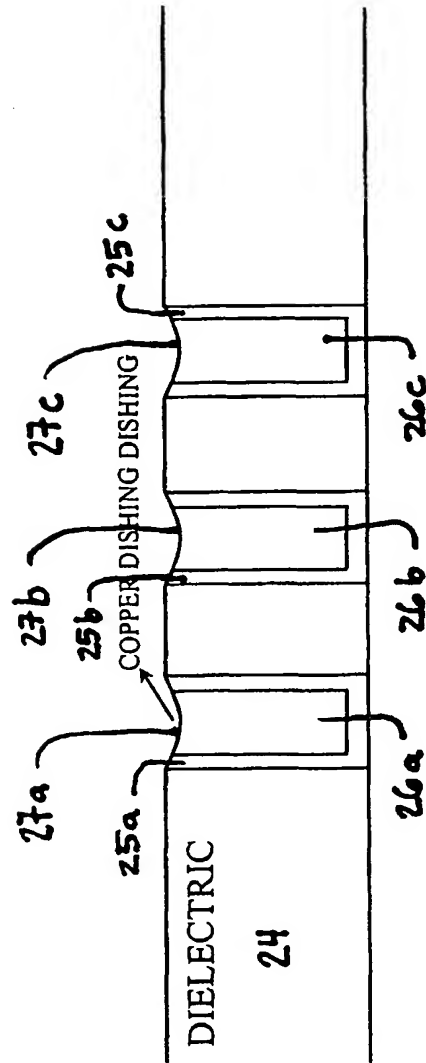


FIG. 4

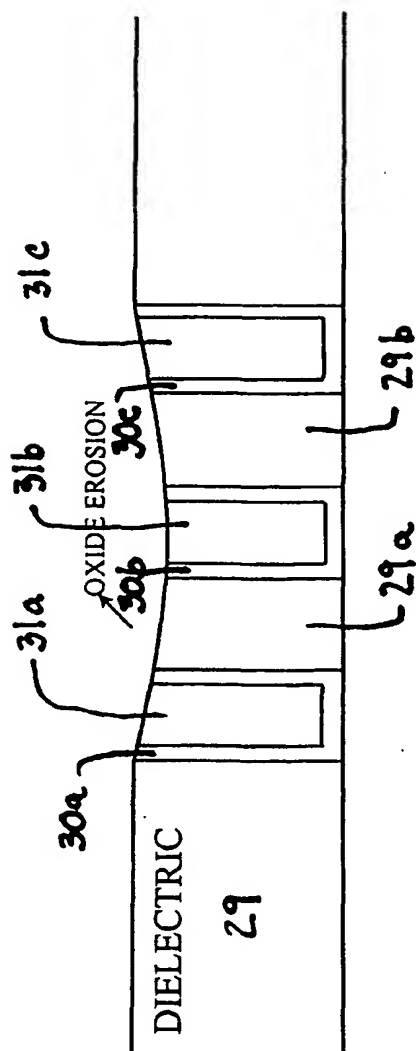


FIG. 5

Spherical Precipitated Silica-13 NM

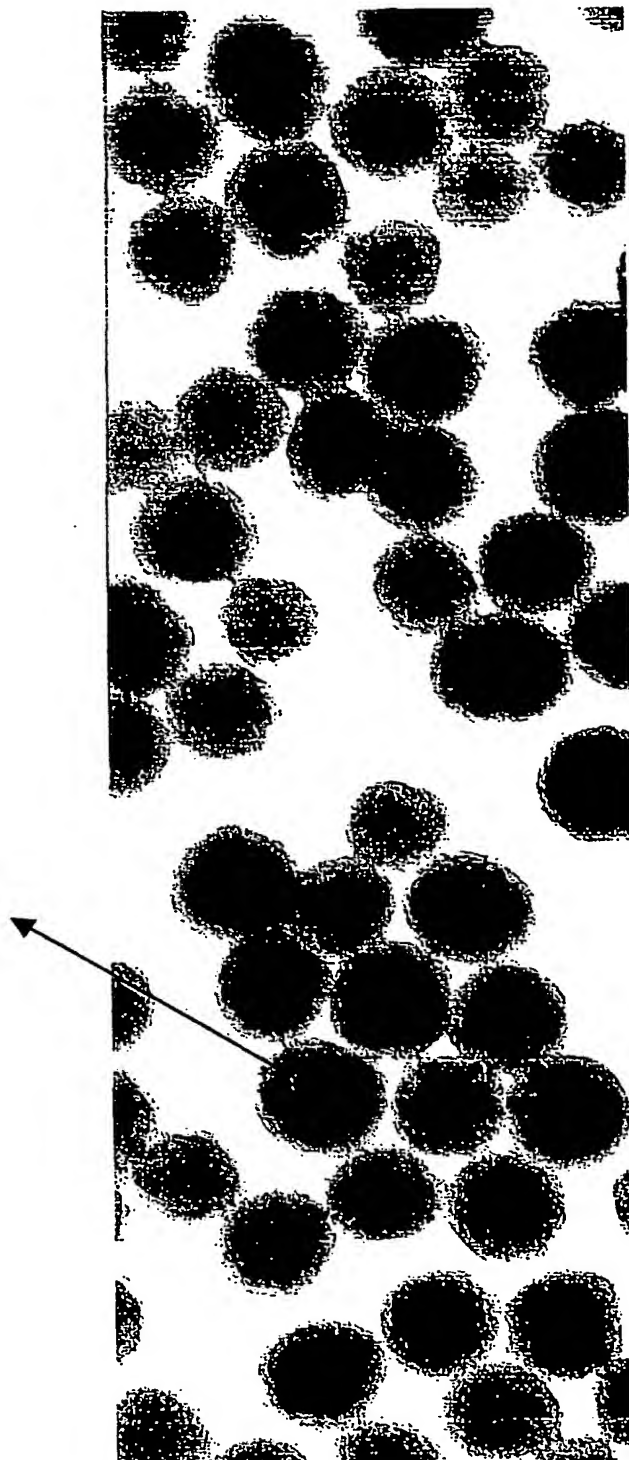


FIG. 6

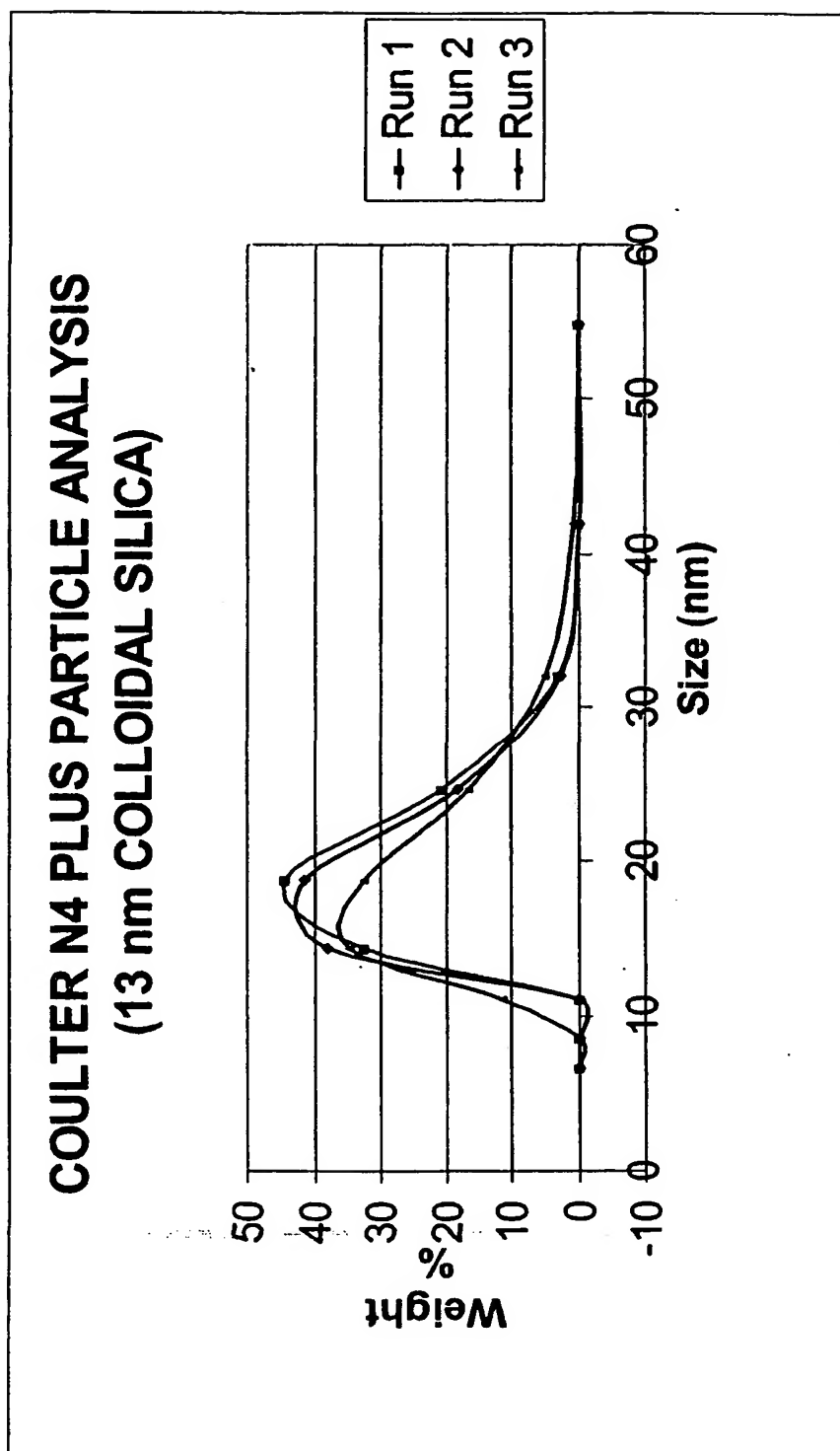


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/13896

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 3/14; C09G 1/02; H01L 21/00; B24B 1/00

US CL : 51/307, 308, 309; 106/3; 438/692, 693; 252/79.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 51/307, 308, 309; 106/3; 438/692, 693; 252/79.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 6,083,840 A (MRAVIC et al.) 04 July 2000, see entire document.	1-101
Y,P	US 6,063,306 A (KAUFMAN et al.) 16 May 2000, see entire document.	1-101
Y	US 6,001,730 A (FARKAS et al.) 14 December 1999, see entire document.	1-101



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 JULY 2001

Date of mailing of the international search report

07 AUG 2001

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